

THERMALLY ACTIVATED GLASSY CARBON - A MATERIAL FOR SUPERCAPACITOR ELECTRODES

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Glassy carbon is a promising material for supercapacitor electrodes. To fully exploit their potential for various applications, we investigated activation processes and the electrochemical properties of various GC electrodes. We find that thermal activation of K-type GC is a favourable process.

1 INTRODUCTION

There is a number of promising materials for applications in high energy and power density electrochemical double layer capacitors (EDLC). One of them, for instance, is ruthenium oxide, which exhibits excellent energy and power densities, but is quite expensive. Carbon, in general, is inexpensive and thus suitable for capacitors for a consumer market.

Glassy carbon (GC), also known as “vitreous” or “polymer” carbon, is prepared by thermal degradation of organic polymers in neutral atmosphere [1]. GC has pores and voids, which can be analyzed by Small Angle X-Ray Scattering (SAXS) experiments [2]. The pores, which are about down to 1 nm in size, can be opened by different activation processes. The high porosity of *activated* GC is linked with a very large internal surface area, which is accessible for a liquid electrolytes, which makes it attractive as an electrode material for EDLC.

The concept of thermal activation of GC for supercapacitor applications was first established by Siemens [3], but not developed anymore.

2 EXPERIMENTAL

We studied commercial disc-like GC, which was pyrolyzed from phenolic resins at various temperatures (K-type 1000°C; G-type 2200°C). Before any further treatment of the material, the structure of the samples was investigated with x-ray diffraction (XRD) and SAXS. The samples were then activated in a furnace at a fixed temperature for a certain time, using either air, oxygen or a gas mixture as oxidant. The internal surface area of the samples was determined with nitrogen adsorption experiments (BET). To investigate electrochemical properties, cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) were recorded, using sulfuric acid as an electrolyte. The thickness of the active film was determined with a scanning electron microscope (SEM) and optical microscopy. Finally, we applied x-ray photoelectron spectroscopy (XPS) to analyze the samples for surface functional groups.

3 RESULTS

3.1 Structure

The results of the SAXS measurements in Figure 1 clearly show, that the K-type GC has smaller pores than the G-type. For K-type we find 7.6 Å for the pore

radius R (G-type 13.0 Å). The pores are very probably polyhedra bounded by graphitic layer planes [4]. In SAXS data analysis we assumed spherelike pores with radius R. The scattering intensity can be described within the Guinier approximation

$$\frac{d\sigma}{d\Omega} = \Delta n_f^2 N V^2 \cdot \exp\left(-\frac{Q^2 R_g^2}{3}\right). \quad (1)$$

Q is the scattering vector, Δn_f^2 is the scattering contrast, and R_g is the radius of gyration; for spheres, R equals $R_g \sqrt{5/3}$.

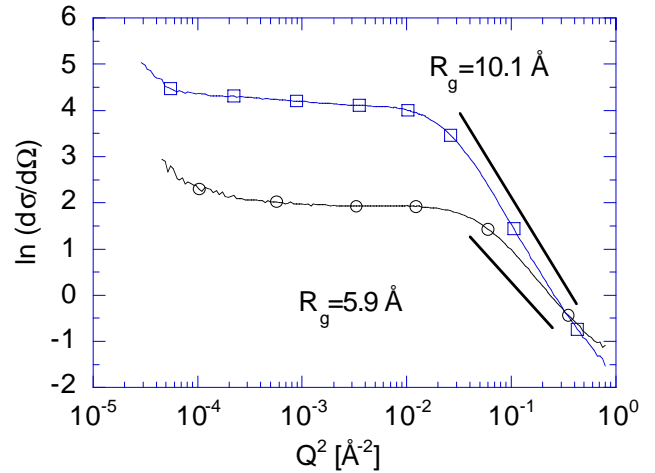


Fig. 1: Guinier plot of non-activated GC K-type (open circle) and G-type (open square). The slope in the Guinier regime is the Guinier radius R_g .

The pore sizes agree well with results found in literature [5]. Number of pores N, pore size distribution, pore volume V and porosity, which strongly affect the electrochemical properties of GC supercapacitors, can also be estimated with SAXS [6]. By ordinary XRD diffraction we verify that the stack height of the graphene sheets and thus pore size depends on the high temperature treatment during pyrolysis.

3.2 Electrochemical properties

The double layer capacitance C of non-activated and smooth GC is about 20 $\mu\text{F}/\text{cm}^2$. This value is confirmed in our measurements (EIS). From the imaginary part of the impedance Z in EIS, we estimated C of the samples using the following relationship:

$$C = \frac{-1}{\omega \cdot \text{Im}(Z)}. \quad (2)$$

Thermally activated K-type samples have values that are more than 4 decades higher. The increase of capacitance with activation time and temperature is displayed in Figure 2a.

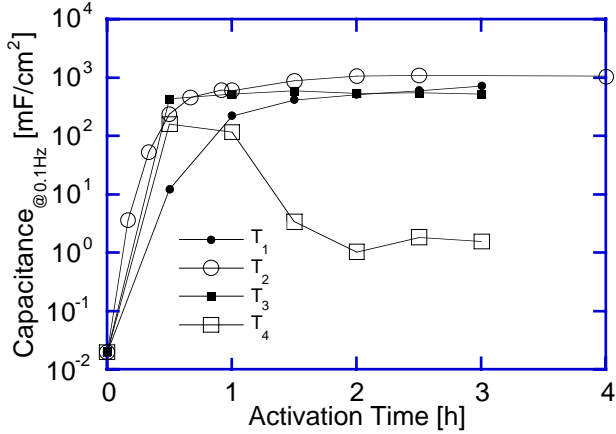


Fig. 2a: Capacitance of K-type GC for various activation temperatures and activation times.

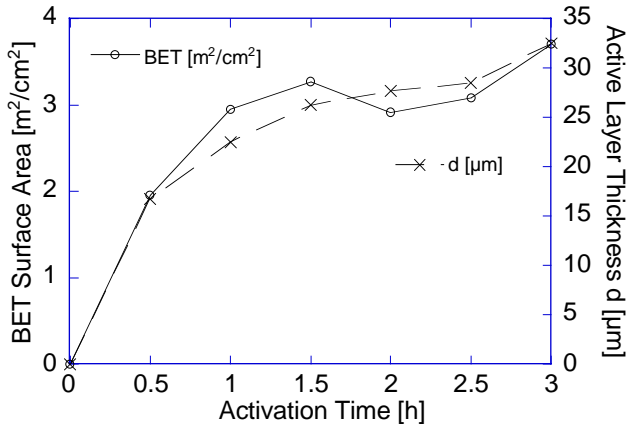


Fig. 2b: Growth of active layer and BET surface have the same trend as the increase of the capacitance.

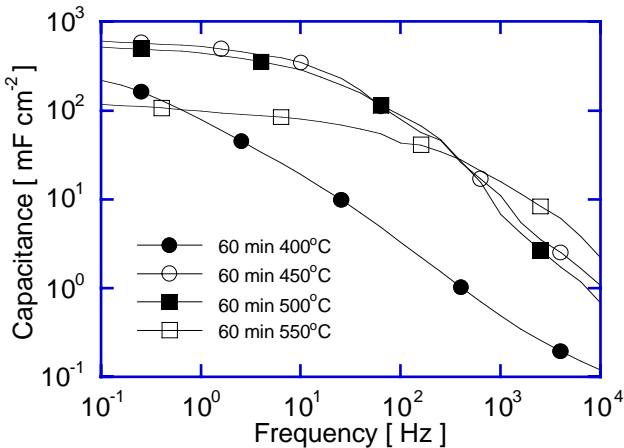


Fig. 2c: Frequency dispersion of capacitance for K-type samples, activated at different temperatures.

At the initial stage of the activation there is a steep increase of C. Then a saturation level is reached. This is in line with the BET measurements and active layer thickness determination, as displayed in Figure 2b.

At temperature T_4 , there is a remarkable burnoff of active layer on the sample, causing a drastic decrease

of C. However, samples prepared at T_4 have a comparatively good frequency response up to 1 kHz (Figure 2c), which is a very interesting feature for high frequency applications.

We found that changing of the composition and the concentration of the oxydant can influence the activation process drastically.

For supercapacitors, also the specific resistance R of the electrode material is an important quantity. GC as an electrode material is a reasonable choice, because of its good electronical conductivity. An additional resistance occurs in the active layer of GC due to diffusion limitation near the solid-liquid interface. We can minimize this resistance by the proper choice of the activation parameters.

Using thermal activated GC electrodes, we recently succeeded in developing a 5 Volt supercapacitor stack prototype with an energy density of 457 J/l and a power density of 33.7 kW/l (stack resistance 24.2 mΩ, capacitance 0.28 F).

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5 REFERENCES

- [1] F.C. Cowlard, J.C. Lewis, Journal of Materials Science **2**, (1967), 507-512.
- [2] W.S. Rothwell, J. Appl. Phys. **39**, 1840, (1968).
- [3] J. Miklos, K. Mund, W. Naschwitz, German Patent DE 30 11 701 A1 (1980), patent holder: Siemens AG.
- [4] R. Perret, W. Ruland, J. Appl. Cryst. **1**, 308, (1968).
- [5] G.M. Jenkins, K. Kawamura, "Polymeric carbons-carbon fibre, glass and char", Cambridge University Press (1976).
- [6] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, O. Haas, to be published.